OTS: 60-41,368

JPRS: 4045

16 September 1960

PHYSICOCHEMICAL INVESTIGATION OF THE

SiC-B4C SECTION OF THE Si-B-C SYSTEM

By A. A. Kalinina
and
F. I. Shamray

- U S S R -

Distributed by:

OFFICE OF TECHNICAL SERVICES
U. S. DEPARTMENT OF COMMERCE
WASHINGTON 25, D. C.

20000717 157

U. S. JOINT PUBLICATIONS RESEARCH SERVICE
205 EAST 42nd STREET, SUITE 300
NEW YORK 17, N. Y.

DTIC QUALITY INSPECTED 4

NOTICE

PHYSICOCHEMICAL INVESTIGATION OF THE
SiC-B4C SECTION OF THE Si-B-C SYSTEM

-USSR-

[Following is a translation of the article "Fiziko-khimi-
cheskoye issledovaniye razreza SiC-B4C sistemy Si-B-C"
by A.A. Kalinina and F.I. Shamray in Doklady Instituta
Metallurgii imeni A.A. Baykova (Works of the Institute
of Mettalurgy imeni A.A. Baykova), No 5, Production
Metallurgy, Physical Metallurgy, and Physicochemical
Methods of Research, Moscow, 1960, pages 151-155.]

It is generally known that compounds of silicon and boron
with carbon (silicon and boron carbides) are widely used by
industry as refractory and wear-resisting abrasive materials.

Boron carbide is at present employed in the nuclear in-
dustry, and silicon carbide is acquiring great importance
as a base for the manufacture of heat-resistant parts of
gas-turbine and jet-plane motors. Articles without binder
(self-sintering) (1) and with a binder of silicon nitride or
boron nitride or carbide are made of it (2). However, these
compounds are not the best materials of the Si-B-C system
for these areas of use. This is to be explained by the in-
adequate study made of the Si-C, Si-B, B-C and especially
the Si-B-C systems.

Of these dual systems, the B-C system has been studied
most thoroughly (3-12).

In 1953, Post, Glazer and Moskovets, on the basis of an
X-ray examination, and also as a result of the study of the
electric resistance and specific weight of boron and carbon
alloys conjectured the presence in the system of solid solu-
tions of carbon in boron. In the investigations made by
Zhdanov, Zhuravlev and Zevin in 1953, and especially in the
works of Zhdanov, Zhuravlev and Samsonov (1954) it was
assumed that B4C dissolves boron, the solubility being

being realized through the substitution of boron for the carbon atoms (central) of the linear chain $C-C-C-B_{12}C_3$ with formation of boron carbide of the composition $B_{13}C_2$ in case of full substitution.

As a result of investigation (13) the first experiment in constructing a phase diagram of this system was proposed. However, the main questions relating to this diagram remained unsolved. There was no definitive solution of the questions of the amount and composition of the compounds of the system, or the nature and limits of the solid solutions based on these compounds.

The B-Si and Si-C systems have been poorly studied. The small amount of data in the literature and their contradictoriness are to be explained by the immense difficulties encountered in making such investigations.

The high melting points of the refractory metals and the alloys, the consequent difficulties due to volatilization of the several components and the alteration of the compositions considerably complicate the methods of experimentation and render difficult the application of N.S. Kurnakov's thermal analysis in its classic form.

The present work was done for the purpose of studying the SiC-C-B4C section of the triple system Si-B-C. In preparing the samples, a press oven of the design worked out at the VNIIASh (14) was used (Fig. 1). This permits samples with a porosity not exceeding 10% to be obtained by the hot-pressing method. Powdered silicon, boron and, in addition, silicon and boron carbides were used as the basic materials.

The amorphous boron obtained magnesium-thermally, contained 95.5% B. The silicon content in the silicon powder was 99.7%. The quantity of admixtures in the silicon and boron carbide powders did not exceed 1%. In view of the fact that, owing to the volatilization of silicon and boron, sintering produced a change in the composition of the alloy, the prescribed composition was insured by the choice of charge.
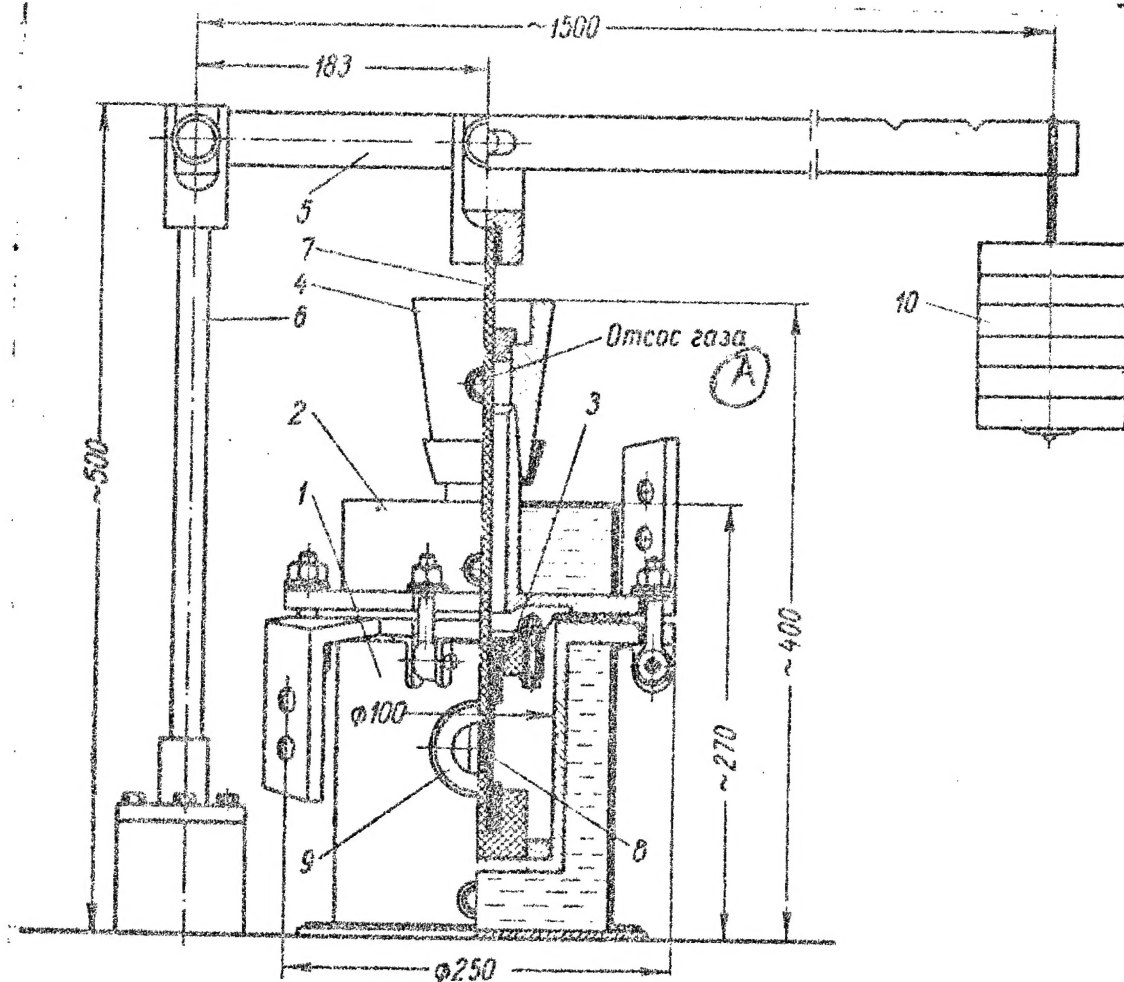
Fig. 1. Experimental Press Oven:

1. water-cooled body; 2. roof with water cooling;
3. carbon heater; 4. hood for pumping out gases;
5. lever; 6. pillar for fastening lever; 7. carbon
punch; 8. sample; 9. inspection window; 10. weight.

Legend: A = gas exhaust.

The samples were prepared in the press oven by a double sintering of the mixtures of the initial components with subsequent roasting of the obtained samples at 2000° for 15 minutes and hardening. In this matter, 21 mixtures were sintered, with 5-10 samples of each composition. The compositions of the alloys studied are shown on the concentration triangle (Fig. 2). Investigation of the samples obtained was done by physicochemical analysis methods. The thermal analysis of the alloys was done by two methods. The first consisted in determining the melting point of the alloys from their deformation. For this purpose, the finished sample in the form of a hollow ring was placed in the heating tube of the press oven, forced down to the lower contact by pressing the lever and was heated by passing a current through it.
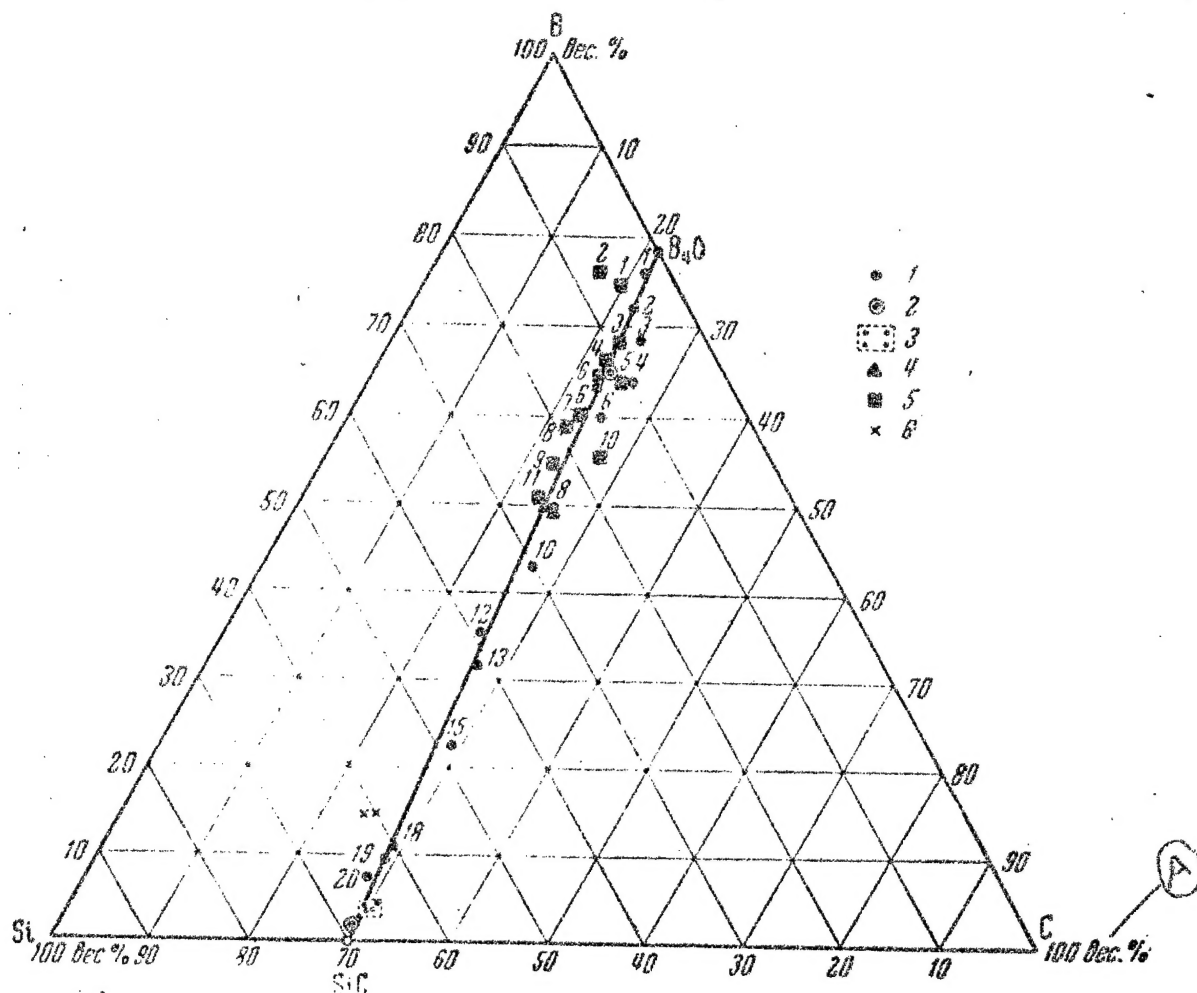

Fig. 2. Concentration Triangle of Compositions:

1. compositions; 2. saturated solutions α and β, secreted chemically; 3. solid α-solution; eutectic; 5. productional samples; 6. Gangler data.
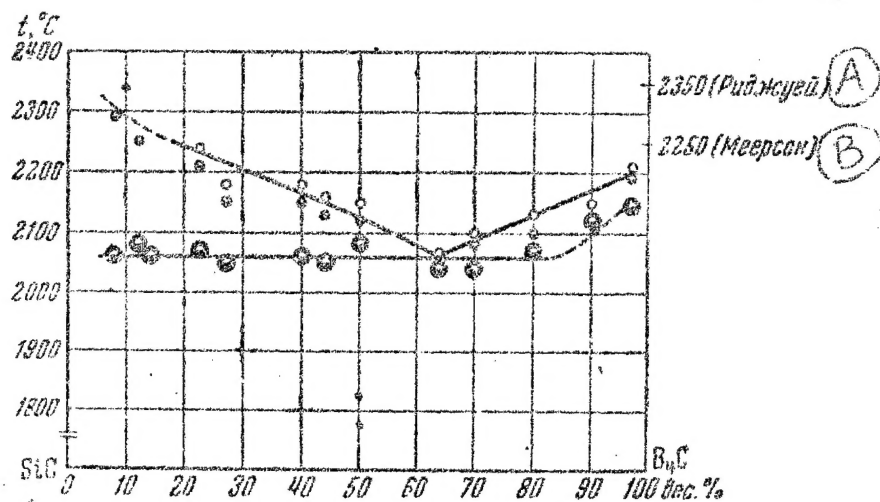Legend: A = weight

Fig. 3. Diagram of state of SiC-B₄C section.

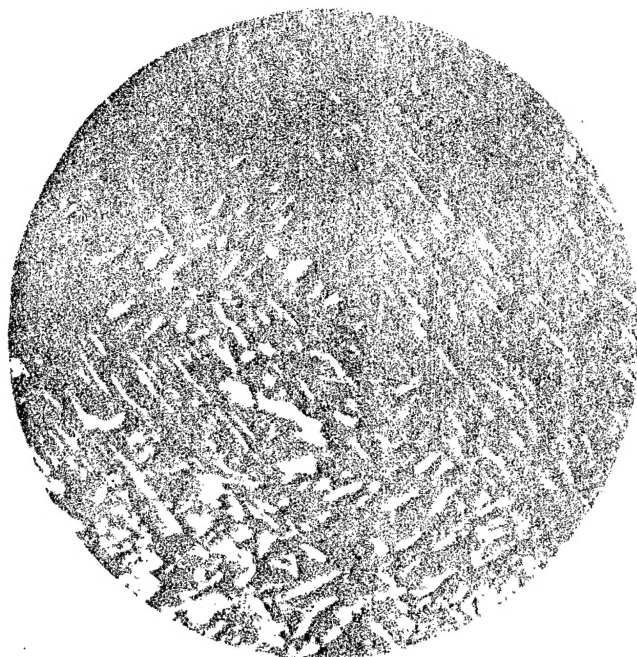Legend: A = (Ridgeway)
        B = (Meyerson)
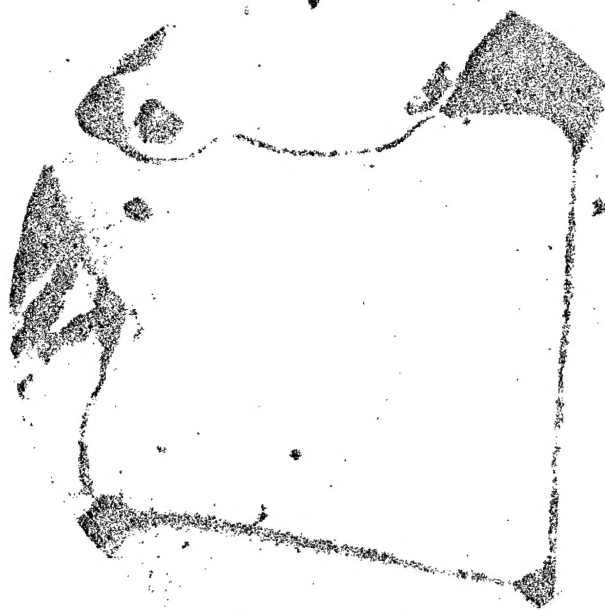
Fig. 4. Eutectics: 35--36% SiC, 64--65% B$_4$C

Fig. 5. Solid α-solution: 68% Si, 2--3% B, 29% C

Fig. 6. Solid β-Solution: 12--13% Si, 64--66% B, 22--23% C

At the moment when melting began there was a deformation of the sample and a lowering of the lever. The change in the temperature of the sample was determined by an optical pyrometer through the aperture in the heating tube. Continuous measurement of the temperature every 15 seconds permitted us to detect the temperature halt caused by the melting of the alloys. Then the melted samples were subjected to examination in slides. In this way, the melting point of the crystals of the primary phase was established.

The microstructure was studied on polished, etched slides by looking through them in reflected light in metallo-microscope MIM-6. The electric resistance was measured with a Wheatstone bridge. The phase X-ray analysis was made by the Debay powder method, and the Zags reverse reflection method was used in determining the lattice parameters. The phase chemical analysis was based on a selective oxidation of the alloys with subsequent dissolving of the oxidized phase in water acidified with hydrochloric acid.

The investigations permitted us to establish the character of the processes taking place in the interaction of silicon, boron and carbon in the SiC--B4C section of the Si B-C system and to construct a diagram of the state of

.'this section (Fig. 3).

It follows from an examination of the diagram that the SiC-B₄C system contains a dual eutectic of the composition 35--36% SiC and 64--65% B₄C with a melting point of 2070° ± 20° (Fig. 4). The eutectic composition found confirms Ton's [Tone?] data obtained by him when using other initial materials (3). The presence of eutectic is observed in the alloys in the composition intervals between 17 and 95% silicon carbide.

In the areas adjacent to boron and silicon carbides lie the fields of the solid α - and β -solutions (Figs. 5 and 6). The solid solutions possess a higher electric resistance than the initial silicon and boron carbides a polygonal structure and altered lattice parameters of the basic initial components.

The supposition that boron carbide can form solid solutions with boron was expressed by Ridgeway as early as 1934. Later, this was confirmed by a number of other investigators (Allen, Zhdanov, Sevast'yanov and others). The physico-chemical investigation showed that in the triple system Si-B-C the area of homogeneity of the alloys in the SiC-B₄C section extends to an 11-12% (by weight) Si content on the B₄C side and to 3% B on the SiC side. In alloys with a silicon content of over 50% by weight, the silicon carbide forming the solid α -solution corresponds in structure to the SiC_III of hexagonal modification. In alloys containing less than 50% silicon by weight, the silicon carbide crystallizes in cubic form (β -SiC). The maximum concentration of solid α - and β -solutions for the above cited experimental conditions was determined by phase chemical analysis. The solid α -solution of the saturated concentration has the composition: 68% Si, 2-3% B, 29% C; the solid β -solution: 12-13% Si, 64-66% B, 22-23% C. These data permit one to regard the SiC-B₄C section of the Si-B-C system as quasibinary, representing a system of solid α - and β -solutions with limited solubility.

CONCLUSIONS

1. The SiC-B₄C section of the Si-B-C system is quasibinary and formed by solid solutions with limited solubility: the solid solution α on the basis of a SiC compound and a α -solid solution on the basis of a B₄C compound, forming a euctectic between them when the SiC content is 35-36% and the B₄C content 64-65% with a melting point of 2070° ± 20°.

-8-

2. at 2070° the β-solid solution on the basis of a B_4C compound extends in the section to a concentration of 15-17% SiC (B = 64 - 66%, Si = 12-13% and C = 22-23%); the solid solution α on a SiC base is considerably lower. In it there is only 4-5% B_4C (B = 2-2.8%, Si = 68%, C = 28%).

LITERATURE

1. K. A. Allegro and L. B. Koffin [Coffin?]: J. Am. Cer. Soc., 39, 415, 1956.
2. Kilmar and Roten: Ceramic Ind., 66, No. 5, 1956.
3. F. Ton [Tone?]: Ind. a. Engin. Chem., 30, No. 2, 1938.
4. Muassan: Compt. Ren. 114-392, 1892; 556, 1894.
5. Podszus. Z. anorg. allg. Chem., 211, 41-48, 1933.
6. Laves [Lawes?]: Z. ges. Wiss. Gottingen Neue Folge, 1, 57, 1934.
7. Ridgeway: Electrochem. Soc. Trans. No. 66, 117-132, 1934.
8. Allen: J. Amer. Chem. Soc., No. 14, 3582, 1953.
9. F. Glazer [Glaser?] and D. Moskovets [Moskowec?]: J. appl. Phys., 14, No. 6, 1953.
10. B. F. Ormont: Struktura neorganicheskikh veshchestv (Structure of Inorganic Sustances), 1950.
11. G. A. Meyerson, G.V. Samsonov: Izv. Sekt. fiz-khim. analiza AN SSSR, 22, 1953.
12. G. S. Zhdanov, G.A. Meyerson, N.N. Zhuravlev and G. V. Samsonov: Zh. fiz. khimii, 28, Issue 6, 1954.
13. G.V. Samsonov, N.G. Zhuravlev, and I. G. Amnuel': Fizika metallov i metallovedeniye (Physics of Metals and Metal Working), 3, Issue 2, 1956.
14. A.A. Kalinina, I.V. Dombrovo. Abrazivy (Abrasives), Issue 21, 1958.
15. V. I. Kudryavtsev. Abrazivy (Abrasives), Issue 18, 1957.

10,002   -END-